UTILIZATION OF WASTE

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APPLICATION OF MAGNESIUM-BEARING TECHNOGENIC RAW MATERIAL IN THE PRODUCTION OF DECORATIVE-FINISHING CERAMICS

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Apodunitic serpentinite byproducts are investigated. It is shown that magnesium-bearing technogenic raw materials can be used with low firing temperatures to obtain decorative-finishing articles with satisfactory physical and mechanical properties — tile for interior wall facing and facades, unglazed and glazed tiles, and ceramic brick.

According to the "Affordable Housing" national target program the most important problem of advancement in the construction sector is the creation of effective resource- and energy-conserving technologies for producing modern high-quality competitive building materials, including ceramic decorative-finishing articles (facing tiles, unglazed and glazed tiles, and others). However, the lack of reserves of high-quality clays in the country and, as often happens, the lack of technologies that would make it possible to manufacture competitive products from low-grade raw materials are holding back the development of domestic decorative-finishing building ceramic. The problem of increasing production efficiency in the ceramic materials subsector is usually solved by bringing into the technological process additives to be used for different purposes and, less often, unconventional mineral raw materials, whose use has become profitable because of efficient technologies that have been developed or because of additional research on the properties of the raw materials.

More than 100 deposits of clayey raw materials of different quality have been surveyed and are being developed in Orenburg Oblast'. Taking account of the commercial reserves, degree of development, and closeness to roads the most promising deposits are Kumakskoe, Dombarovskoe, Chernorechenskoe, and others. However, even though substantial and diverse natural reserves of clayey raw material exist and the deposits are economically secured, the region has no enterprises that manufacture ceramic tiles or high-quality brick, including facing and unglazed tiles. The demand for such decorative-finishing building ceramics is met by importing these materials from other regions of the country or from neighboring and distant foreign countries.

The possibility of obtaining ceramic facing material based on raw materials from the Southern Ural region is being studied at Orenburg State University in order to organize the local production of ceramic tiles and to utilize byproducts of the production process.

Moderately plastic clay from the Chernorechenskoe deposit was chose for these investigations. With respect to their mineral composition the clays from this deposit are mixed-layer formations with chlorite-hydromica composition and an admixture of quartz and feldspar. This is supported by integrated differential thermal analysis (Fig. 1*a*). The nonplastic fraction of the clays is of the order of 30%.

The refractoriness of the clays varies from 1180 to 1200°C. The air-dry shrinkage is 8.1 – 9.3%, and the total shrinkage is 8.2 – 9.5%. The maximum sintering temperature is 1150°C. The sensitivity of the clay to drying is average (the coefficient of sensitivity to drying > 1.00 – 1.24).

The chemical composition of the clays is presented in Table 1.

Now there is a special urgency to using technogenic initial materials in the production of ceramic materials, since the construction industry is the most materials-intensive in-

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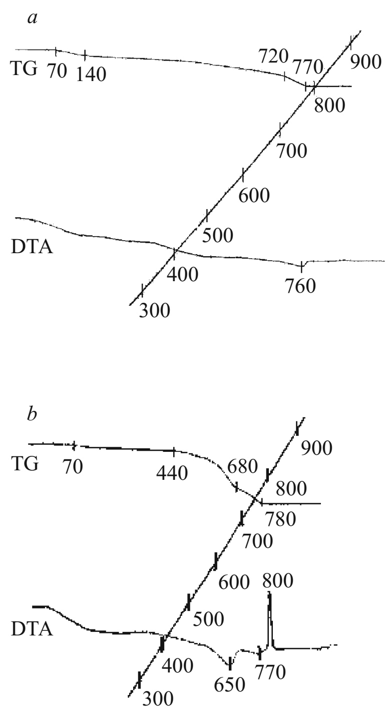

Fig. 1. DTA of clays from the Chernorechenskoe deposit (*a*) and apodunitic serpentinitic byproducts (*b*).

dustrial sector, capable of processing millions of metric tons of mineral raw materials, including byproducts of the mining – enrichment industry.

Previous investigations [1] have shown that mining byproducts containing magnesium silicates and obtained from processing raw materials in the form of a pulverized mineral mass (powder, sand, crushed rock) are a promising initial material for manufacturing various building materials, including ceramic construction articles, and can replace conventional raw materials in articles made from mixes with only a few components.

Petrographic analysis of magnesium-bearing byproducts present in tailings in Orenburg Oblast' has established that with respect to mineral composition these are water-free and water-bearing magnesium silicates: dunites, apodunitic serpentinites, serpentinites, and pyrophillitic associations. To obtain ceramics with prescribed properties and improve the sintering process, apodunitic serpentinites — byproducts from the Khalilovskoe Mining-Enrichment Works (Southern Urals, Orenburg Oblast') — were introduced into the mix.

The effect of the byproducts, containing magnesium silicates from the mining-enrichment works on the technological properties of decorative-finishing ceramic articles — strength, density, water absorption, total shrinkage with low-temperature calcination — was studied for the example of apodunitic serpentinites.

First, the particularities of the mineral composition of serpentines from the Khalilovskoe deposit were studied. Petrographic analysis, performed jointly with "Orenburg-geologiya" JSC, showed that the main rock-forming mineral is serpentine (66 – 77%[2]), which cements and replaces relict olivine grains, comprising 20 – 25%. Magnesite (0.5 – 5%), chromium spinel (2 – 3%), and magnetite dust (0.5 – 1%) are also encountered in the smaller quantities indicated. The chemical composition of the serpentine-bearing technogenic initial material is presented in Table 1; a thermogram of the material is displayed in Fig. 1*b*.

Analysis of the thermal effects on the DTA curve confirms that the main rock-forming mineral is serpentine. Three endothermal effects are recorded in the heating range from 20 to 1000°C (very weak in the temperature intervals 70 – 140 and 830 – 900°C and intense for 600 – 700°C).

The fact that the third (weak intensity) endo effect occurs in the same temperature interval as the stronger exothermal reaction is an indication of the structural imperfection of serpentine. In this connection, a third endo effect does not ap-

[2] Here and below — content by weight.

TABLE 1.

Deposit	Content, wt.%									
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	ΣR_2O	Cr_2O_3	MnO	NiO	calcination losses
Chernorechenskoe	60.57	11.27	4.70	2.42	8.74	3.23	–	–	–	9.07
Khalilovskoe	38.07	1.92	6.94	37.73	0.51	0.05	0.37	0.11	0.22	14.08

TABLE 2.

Mix component	Content, wt.%									
	1	2	3	4	5	6	7	8	9	10
Clay	100	90	80	70	60	50	40	30	20	10
Serpentinite-bearing technogenic initial material	–	10	20	30	40	50	60	70	80	90

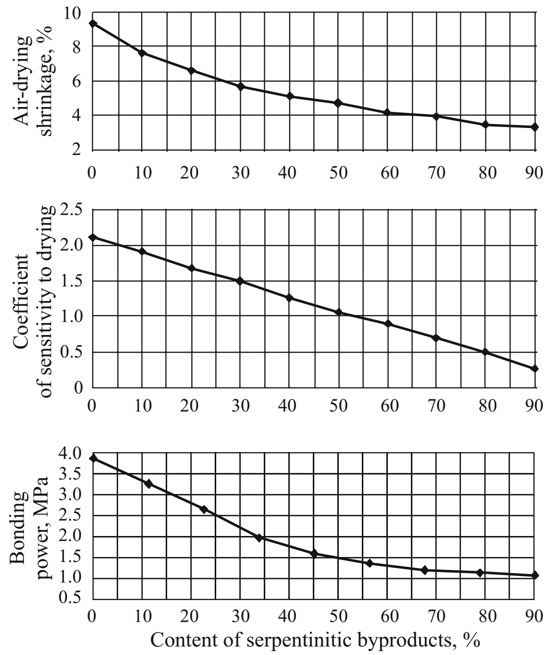

Fig. 2. Dynamics of the variation of the pre-firing properties of articles as a function of the content of serpentinitic byproducts in the mix.

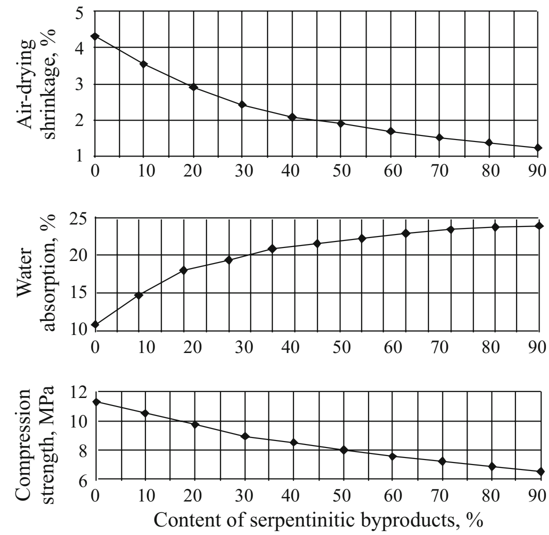

Fig. 3. Dynamics of the variation of the firing properties of articles as a function of the content of serpentinitic byproducts in the mix.

pear on the DTA curve of the experimental technogenic raw material. The second endo effect attests to the destruction of the structure of the mineral serpentine with an OH group removed at the same time. A sharp jump, equal to 0.4%, of the mass losses is recorded in the TG curve at temperature 650°C.

With further heating to 790 – 810°C new crystal phases are formed from the products of the destruction of the crystal lattice: forsterite (crystalline) and enstatite (x-ray amorphous). These processes are confirmed by an exo effect on the DTA curve and by XPA data. The petrographic analysis of the sample fired at 1300°C attests to a transition of enstatite into protoenstatite with simultaneous secondary recrystallization.

In summary, heat-treatment of the apodunitic serpentinitic byproducts engenders complex processes that change the phase composition and structure of the byproducts. Similar phase formation processes occur with heat treatment of chemically pure magnesium oxide in the production of refractories and technical ceramic articles. This fact and analysis of the processes occurring in the system SiO_2 – Al_2O_3 – MgO suggest the possibility of using magnesium-bearing rocks in the technology for obtaining construction ceramic articles, glazes and pigments for them, and an active role of technogenic and magnesium-bearing raw materials in the production of ceramic and the formation of the technological properties of the articles.

The initial materials were weighed out, finely ground in a laboratory ball mill to residue 1 – 3% on a No. 0315 sieve, and moistened, after which molding pastes with moisture content 18 – 24%, depending on the plastic component fraction in the charge were prepared (Table 2). The prepared mixes were moistened in the course of a day and subjected to molding. The dried samples were sintered in a laboratory furnace at 1050°C.

The soaking time at the maximum temperature was 30 min for the flat samples and 2 h for cubic samples. A standard program was used to analyze the experimental results. For each of these compositions, the pre-firing properties (air-drying shrinkage, coefficient of sensitivity of the clays to drying, the bonding power of the clay substance) and the firing properties (fire and total shrinkage, water absorption, and compression strength) were determined.

As Fig. 2 shows, increasing the fraction of the magnesium-bearing technogenic initial material in the charge makes it possible to improve the drying properties of the articles substantially. The sensitivity of a green article to drying decreases by almost 50%, and the primary shrinkage deformations which are most dangerous decrease by 40 – 50%. This makes it possible to change the drying regime — to accelerate it. However, increasing the fraction of technogenic initial material in the charge decreases the bonding power of the clay component at the formation stage but the mechanical strength of the articles (green part) is found to be adequate in this case for moving the article along the process line for further processing.

The dynamics of the variation of the properties of the articles after firing at temperature 1050°C (Fig. 3) attests to the possibility of obtaining articles with water absorption 16 – 17% and ultimate compression strength 10.0 – 10.8 MPa with the introduction of 10 – 15% magnesium technogenic initial material. Further increasing the firing temperature without changing the firing time makes it possible not only to intensify the formation processes for the structure of the material but also to perform modeling of the mix composi-

tion. As the firing temperature of the samples increases to 1100°C, the amount of the technogenic initial material in mixes with water absorption not exceeding 16 – 17% increases to 35 – 40%. For firing in the temperature interval 1150 – 1170°C, the technogenic initial materials fraction in the mixes with the same water absorption increases to 60 – 65%. It should be noted that when the fraction of the technogenic magnesium-bearing initial material in the mix is increased, the mechanical strength of the articles does not decrease. The frost-resistance marker of all compositions fired in the temperature interval 950 – 1170°C was at least 50 cycles.

In summary, it is possible to obtain with low-temperature firing decorative-finishing articles based on magnesium-bearing technogenic initial material with satisfactory physical and mechanical properties — tiles for interior facing of walls and facades, glazed and unglazed tiles, and ceramic brick.

REFERENCES

1. V. A. Gur'eva, *Physical – Chemical Investigations of the Utilization of Dunites in Decorative-Finishing Ceramics* [in Russian], Orenburg (1970).